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Influence of hydrogen on the stability of positively charged silicon dioxide clusters

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Spectra of positively charged secondary ions from thermally grown SiO_2 films were recorded in a time-of-flight secondary ion mass spectrometry scheme. Ablation of cluster ions was induced by the impact of slow (4 keV/u) Au^{69+} projectiles. The intensities of $Si_xO_yH_z^+$, ($x=1-22$, $y=1-44$, $z=0-7$) clusters are found to depend sensitively on the oxygen to silicon ratio and also on the hydrogen content. We find that oxygen rich clusters, $y=2x+1$, and, in one case, $y=2x+2$, can be stabilized by the incorporation of two additional hydrogen atoms in the cluster. © *2000 American Institute of Physics.* [S0021-9606(00)70630-1]

I. INTRODUCTION

The formation and stability of oxide clusters is an active field of research with implications to astrophysics, catalysis, and fundamental surface chemistry.[1–5] Several studies on charged and neutral silicon dioxide clusters in the gas phase have been presented in recent years.[3–5] Laser ablation was used by Xu *et al.*[4,5] and by Lafague *et al.*[3] to study the mass distributions of negatively charged silicon dioxide clusters as a function of laser parameters and the properties of target surfaces. Both Xu *et al.* and Lafargue *et al.* discuss the influence of SiOH defects in porous siliceous materials on the formation and stability of $[(SiO_2)_nOH]^-$ clusters. $(SiO_2)_n^-$ clusters with masses up to 1140 u, corresponding to $n=20$ SiO_2 molecules were detected following laser ablation.[4,5]

Production of positively charged clusters, $SiO_{0-2}(SiO_2)_n^+$ from solid SiO_2 was reported by Imanishi *et al.*, who used 1.4 to 5.3 MeV Ag ions to initiate electronic sputtering.[6] Here, clusters with up to $n=6$ repeat units were detected. Oxygen-rich silicon dioxide clusters dominate spectra of negative secondary ions.[4,5,7] On the contrary, oxygen-rich clusters have not been observed in positive polarity.[6] Negative clusters, $(SiO_2)_n^-$, containing up to $n=24$ SiO_2 molecules were produced by the impact of slow, very highly charged ions on silicon dioxide films on silicon.[7]

In this article, we report on the observation of positively charged SiO_2 clusters that were desorbed from thin silicon dioxide films on silicon by slow (4 keV/u, or 8.7×10^5 m/s), very highly charged gold ions (Au^{69+}). We find that cluster intensities depend on a critical interplay between the number of oxygen and silicon atoms and the number of hydrogen atoms in the cluster. We observe positively charged, oxygen-rich clusters such as $(SiO_2)_2OH_2^+$, $(SiO_2)_8O_2H_5^+$, and $(SiO_2)_{10}OH_2^+$ that are stabilized by the incorporation of additional hydrogen atoms.

II. EXPERIMENT

Highly charged ions were extracted from the Electron Beam Ion Trap (EBIT) at Lawrence Livermore National Laboratory[8,9] and reached the target chamber after momentum analysis in a 90° bending magnet. The EBIT is a compact (few m^2 footprint) source of highly charged ions like Xe^{44+} and Au^{69+}. Currently, beam intensities up to a few million ions per second can be delivered into a 1 mm^2 spot. Positive secondary ions are accelerated by a target bias of +2.4 kV and are extracted into a reflectron-type time-of-flight secondary ion mass spectrometer. The mass resolution, $m/\Delta m$, was about 1000 at $m=28$ u. A more detailed description of the experimental setup can be found in Refs. 9 and 10. In the present study we used a beam of Au^{69+} ions with a kinetic energy of 800 keV.

Targets were 150 nm thick SiO_2 films that had been grown on silicon wafers by standard thermal oxidation. Targets were analyzed both after thermal annealing at 450 °C and without further *in situ* treatment. The pressure in the target chamber was kept at about 5×10^{-9} Torr during analysis.

Electronic sputtering and secondary ion emission from silicon dioxide surfaces following the impact of slow, highly charged ions has been discussed in a number of recent publications.[7,9,11–13] Briefly, the interaction of a highly charged ion with the solid surface is dominated by fast neutralization and de-excitation processes. The potential energy of highly charged ions is the sum of the binding energies of the electrons that were removed when forming the ion. The

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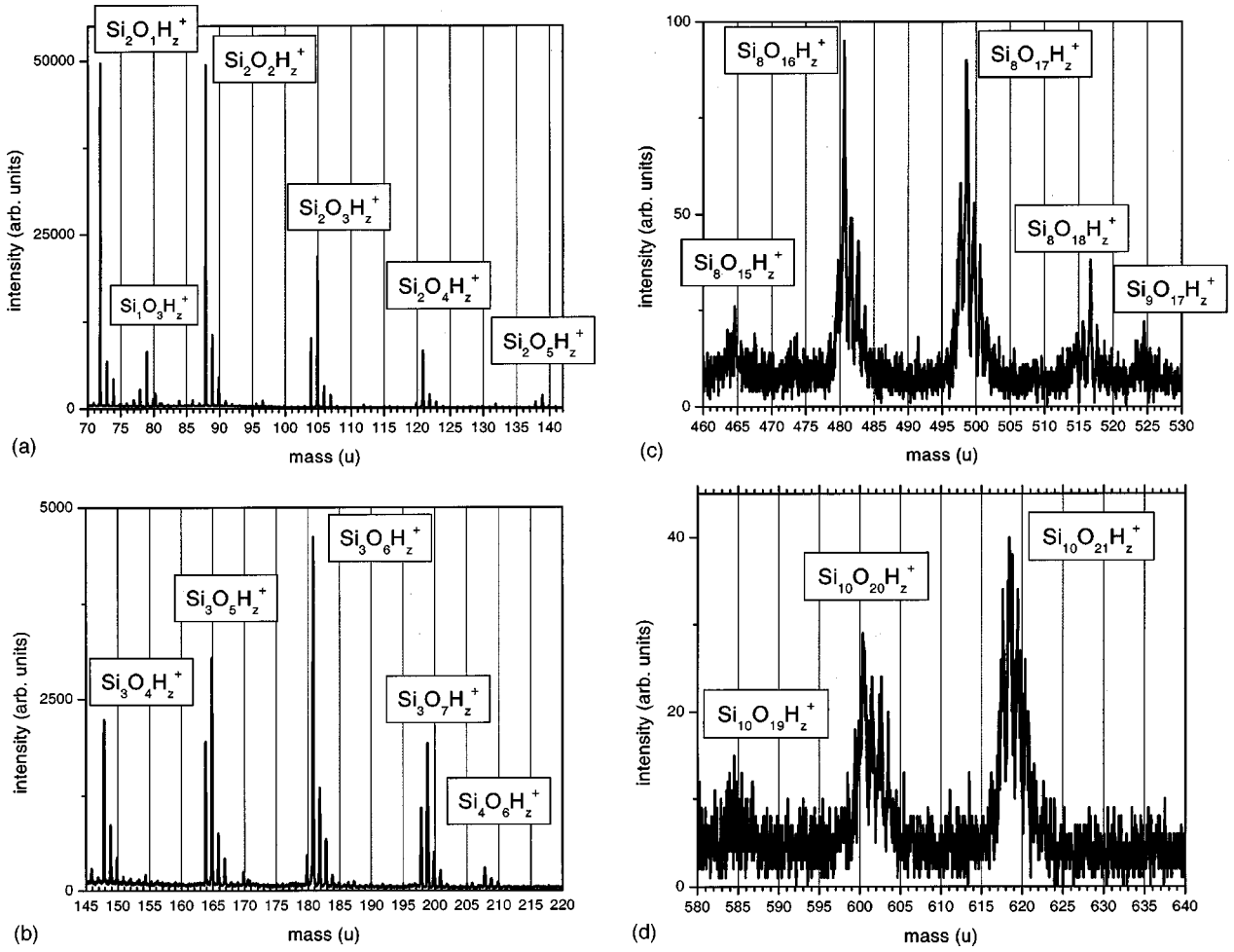

FIG. 1. Sections of time-of-flight secondary ion mass spectra of positively charged silicon dioxide clusters containing two (a), three (b), eight (c), and ten (d) silicon atoms.

potential energy of Au^{69+}—170 keV—is deposited in a time of only 5 to 10 fs close to the target surface into a volume of a few cubic nanometers.[9,14] This intense ($\sim 10^{14}$ W/cm^2), ultrafast electronic excitation of the target material induces sputtering and secondary ion emission. Sputtering yields, secondary ion yields, and in particular, yields of charged clusters in the electronic sputtering of SiO_2 by slow, highly charged ions are over 2 orders of magnitude higher than yields for singly charged projectiles.[9,11,13]

III. RESULTS AND DISCUSSION

Figures 1(a) to 1(d) show sections of a time-of-flight secondary ion mass spectrum with $Si_xO_yH_z^+$ clusters containing 2, 3, 8, and 10 silicon atoms. The first important observation concerns the influence of hydrogen content on the intensity of cluster ions. For clusters with two silicon atoms, Si_2O^+ and $Si_2O_2^+$ are more abundant than the hydrogen-containing clusters Si_2OH^+ and $Si_2O_2H^+$. When one more oxygen atom is added, the hydrogen-containing cluster $Si_2O_3H^+$ is found to be twice as intense as $Si_2O_3^+$. This trend continues for $Si_2O_4H^+$ and $Si_2O_5H^+$. We observe the same effect of hydrogen incorporation on the intensity for larger clusters. For clusters with three silicon atoms, $Si_3O_5H^+$ is more intense than $Si_3O_5^+$, and for ten silicon atoms $Si_{10}O_{20}H^+$ is more intense than $(SiO_2)_{10}^+$. For clusters with stoichiometric oxygen and silicon content, i.e., $(SiO_2)_nH_z^+$ clusters, the hydrogen-containing clusters are consistently found to be more abundant than the bare $(SiO_2)_n^+$ clusters.

Hydrogen is present at the surfaces of thermal silicon dioxide films in the form of SiOH defects and as an ambient contamination. The influence of SiOH and hydroxyl groups on the formation of hydrogen-containing negative SiO_2 cluster ions was discussed by Xu *et al.*,[4,5] and by Lafargue *et al.*[3] To test the influence of this effect, we annealed silicon dioxide films at 450 °C for 30 min. Annealing decreased the relative intensities of hydrogen-containing clusters slightly, consistent with the concept of thermal dehydration.[3] The dominant trends in the data presented above were, however, not affected by the annealing.

Reducing the thickness of oxide films from 150 nm to 100 and 50 nm led to a decrease of the secondary ion intensity[12,15] but had no effect on the dominant spectral features.

The oxygen-to-silicon ratio for which the hydrogen containing clusters are more intense than bare $Si_xO_y^+$ clusters depends on the number of silicon atoms in the cluster (Fig. 2). This ratio converges with increasing cluster size to the value for stoichiometric silicon dioxide.

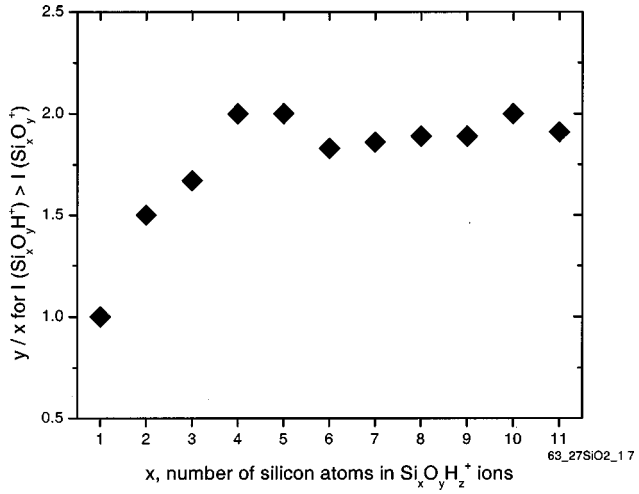

FIG. 2. Ratio of oxygen-to-silicon atoms in clusters for which the hydrogen-containing cluster becomes more intense than the bare $Si_xO_y^+$ cluster as a function of the number of silicon atoms in the cluster, *x*.

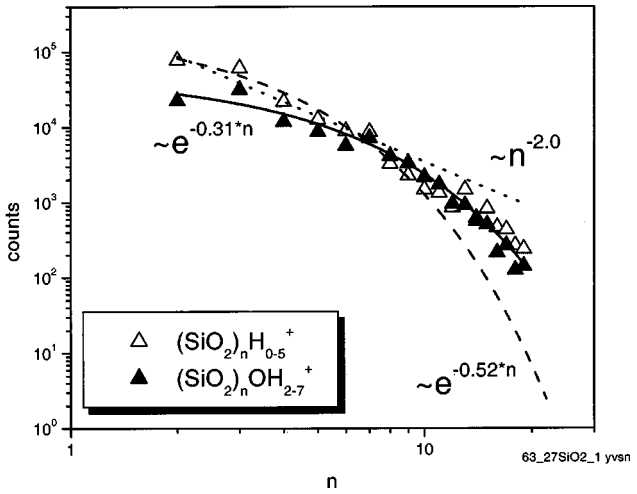

FIG. 3. Intensity of $(SiO_2)_nH_{0-2}^+$ (open symbols) and $(SiO_2)_nOH_{2-7}^+$ (solid symbols) as a function of cluster size, *n*. Dotted line: fit of the $(SiO_2)_nH_{0-2}^+$ intensity to a power law, n^{-2}; dashed line: fit of the $(SiO_2)_nH_{0-2}^+$ intensity to an exponential decay, $e^{-0.31n}$. The solid line is a fit of the intensity of oxygen-rich clusters $(SiO_2)_nOH_{2-7}^+$, to an exponential decay function, $e^{-0.52n}$.

For a given number of silicon atoms, *x*, we observe clusters with $2x$, $2x-1$, and $2x-2$ oxygen atoms. Oxygen-rich clusters with $y=2x+1$ oxygen atoms are observed only when two additional hydrogen atoms are incorporated into the cluster. For example, in Fig. 1(b), we observe $Si_3O_7H_z^+$ only for $z \geqslant 2$, while $Si_3O_7^+$ (196 u) ions and $Si_3O_7H^+$ (197 u) are not observed. This is consistently observed for all oxygen-rich clusters. Interestingly, the intensity of oxygen-rich clusters surpasses that of stoichiometric clusters for clusters containing $x=8$ to 12 silicon atoms. Oxygen-rich clusters with more than one oxygen atom above the stoichiometric content, i.e., $y=2x+2$, were not observed, with only one exception. While peaks of $(SiO_2)_2O_2H_z^+$ at 152 u, $(SiO_2)_3O_2H_z^+$ at 212 u, and $(SiO_2)_{10}O_2H_z^+$ at 636 u are absent in the spectra of Fig. 1, we do observe a sizable contribution of $(SiO_2)_8O_2H_5^+$ at 517 u. This cluster is also stabilized by the incorporation of additional hydrogen atoms.

In Fig. 3, we show the intensities of the two cluster series, $(SiO_2)_nH_{0-2}^+$ and $(SiO_2)_nOH_{2-7}^+$, as a function of cluster size, *n*. The data for the intensities of stoichiometric cluster series are fit to an exponential decay function, $I \sim e^{-\alpha n}$, and to a power law, $I \sim n^{-\tau}$. The former follows a model of cluster formation in the gas phase; the latter is consistent with models assuming emission of clusters as intact entities.[7,16] Neither one of the fits describes the data well, and this indicates that several mechanisms contribute to the formation of these clusters. The data for the oxygen-rich clusters can be fit well to an exponential decay function. This indicates that the additional hydrogen which is necessary to stabilize these clusters is captured and incorporated into the cluster ion when it moves away from the surface. Evidence for a similar hydrogen pickup effect was recently reported for the formation of hydrogen-containing, positively charged carbon clusters from fullerene targets.[17]

In conclusion, we have produced a series of positively charged silicon dioxide clusters from thermal oxide films on silicon substrates in a time-of-flight secondary ion mass spectrometry scheme with highly charged projectiles. We find that cluster ion intensities depend both on the ratio of oxygen and silicon atoms and on the number of hydrogen atoms that are incorporated into a cluster. Comparison with model predictions suggests that oxygen-rich clusters $(SiO_2)_nOH_{2-7}^+$, stabilize by hydrogen incorporation on their path away from the target surface.

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